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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> C03C 13/06, 1/00, 1/02, C03B 1/02	<b>A1</b>	<b>(11) International Publication Number:</b> WO 95/34516 <b>(43) International Publication Date:</b> 21 December 1995 (21.12.95)
<b>(21) International Application Number:</b> PCT/EP95/02109 <b>(22) International Filing Date:</b> 2 June 1995 (02.06.95)  <b>(30) Priority Data:</b> 9412011.0 15 June 1994 (15.06.94) GB  <b>(71) Applicant (for all designated States except US):</b> ROCKWOOL INTERNATIONAL A/S [DK/DK]; Hovedgaden 501, DK-2640 Hedehusene (DK).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SORENSEN, Lone, Moller [DK/DK]; Bistruphave 7B, DK-3460 Birkerød (DK). JENSEN, Søren, Lund [DK/DK]; Tordenskjoldsgade 23, 2.th, DK-1055 København K (DK).  <b>(74) Agent:</b> GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PRODUCTION OF MINERAL FIBRES  <b>(57) Abstract</b>  Man made vitreous fibres are made by a process comprising forming moulded briquettes of particulate mineral material that includes contaminated foundry sand, forming a melt by melting in a furnace a charge comprising the briquettes and forming fibres from the melt, and the melt and the fibres have a content, measured as oxides, that includes Al <sub>2</sub> O <sub>3</sub> in an amount of not more than 4 % by weight.		

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### Production of Mineral Fibres

This invention relates to the production of Man Made Vitreous Fibres (MMVF) that are biologically soluble, that is to say they have an acceptable rate of biologically useful degradation in physiological saline solution.

It is well known to form in a furnace, such as an electric furnace or a cupola furnace, a mineral melt and to use this melt for various industrial purposes. The mineral melt is generally formed from a blend of minerals selected so that they produce a melt having the desired melting point and other properties, having regard to the intended end use. The mineral materials are usually freshly produced or mined materials such as crushed rock or crushed slag and sand.

In EP-A-508589 it is proposed to form a melt from a plurality of solid waste streams that are used in proportions such that the melt has a content within certain defined ranges. Materials that are mentioned for use as this plurality of waste streams are municipal incinerator bottom ash, hazardous wastes incinerator bottom ash, baghouse or precipitator dust, steel plant dust, electroplating sludge, electrochemical machining sludge, waste foundry sands, contaminated soils, dried and contaminated sewage solids, cementitious fixation, coal combustion fly ash, inorganic paint pigment residues and spent refractory materials. The furnace can be a coke-fired cupola furnace of the type used in the grey iron casting industry. The melt is drained from the furnace under conditions that allow separation of free metal from the solution of oxides, which can be poured into moulds or quenched.

When MMV fibres are formed from a melt, the composition of the fibres influences their properties. It is known that the solubility of MMV fibres in physiological saline solutions can be increased by appropriate selection of the composition of the melt. As a generality, best results are obtained when the amount of aluminium in the

melt, measured as oxides, is below 3 or 4% by weight  $\text{Al}_2\text{O}_3$ . Accordingly, if biological solubility is required the mineral material for forming the briquettes, and any additional material that is included in the charge, has to be selected so that it complies both with the required low aluminium content and with the requirement that the melt has appropriate melt properties. Thus the charge must have appropriate melting temperature and viscosity characteristics such that the melt has appropriate fibre-forming properties.

Mineral fibres are generally made by a process comprising forming moulded briquettes of particulate mineral material, forming a melt by melting in a furnace a mineral charge comprising such briquettes and forming fibres from the melt. The components of the mineral charge have to be selected so as to provide a melt having appropriate melt properties and fibre-forming properties and this places constraints on the materials that can be used. When it is desired that the melt should have a low alumina content, this imposes further constraints on the choice of materials for the mineral charge. Materials that have low alumina content and that might be thought to be suitable tend to be rather expensive and some of these materials tend to provide a melt having inconvenient melt properties, for instance a rather high melting point. In practice therefore it is necessary to use very expensive blends of materials for forming biologically soluble MMV fibres, and this represents a serious impediment to the availability of such fibres.

It would therefore be desirable to be able to select minerals that are much more readily available and cheaper and yet which are capable of being used to give a fibre-forming melt having a low content of  $\text{Al}_2\text{O}_3$ .

In the invention, MMV fibres are made by a method comprising forming moulded briquettes of particulate mineral material, forming a melt by melting in a furnace a mineral charge comprising the briquettes and forming fibres

from the melt, and in this method the melt and the fibres have a content, measured as oxides, that includes alumina in an amount of below 4% by weight and the briquettes are formed of particulate mineral material that includes  
5 contaminated foundry sand.

Contaminated foundry sand is foundry sand that has been used for making a foundry mould and that is still contaminated with a substantial proportion of the impurities that are present in the foundry sand after its  
10 use as a foundry mould. Thus it is contaminated with residues of binder, such as phenol formaldehyde resin, furan, bentonite or other foundry binder, and often with residues of metal, from the casting operation. The presence of these various residues has resulted in it  
15 generally being considered that the foundry sand cannot be used for any useful process unless it is first subjected to thermo/mechanical regeneration process comprising the steps of crushing, sieving, washing and incinerating to remove the contaminants and fines. However such reclamation  
20 processes tend to be very expensive and so render the use of the reclaimed sand uneconomic. For instance such a process is described in Mineral Processing No.8, August 1987, pages 456 to 462 by Bauer, where the significant process stages are magnetic separation fluid bed treatment  
25 and counter flow baffling.

In the invention, the contaminated foundry sand is used without significant prior reclamation processes. Indeed, if any reclamation process is conducted, it is usually confined to sieving the sand.

30 Thus the invention simultaneously solves two problems, namely the need to find a way of economically utilising contaminated foundry sand, and the need to find a cost-effective mineral that can be used in a fibre-forming melt designed to produce fibres having low alumina content.

35 One advantage of the invention lies in the fact that it is not necessary to remove fines from the contaminated foundry sand before it may be used. As explained above,

this was previously always considered necessary if the foundry sand was to be useful. Thus particularly economical use of contaminated foundry sand is made possible by the invention.

5 In fact, the presence of fines can be advantageous in the invention. Fines exhibit excellent melting properties in conventionally used melting processes. This is due to their need for shorter residence times at any given melting temperature than larger particle size foundry sand.

10 This feature means that it is possible to use higher amounts of high melting point materials such as contaminated foundry sand in the charge than would otherwise be possible. The presence of fine particle size foundry sand also minimises or eliminates the need to  
15 incorporate fluxing agents, and thus avoids the constraints they place on the choice of chemical compositions.

The amount of contaminated foundry sand is preferably at least 10%, usually at least 20% based on the total mineral charge and often at least 30%. Usually it is not  
20 more than 75%, and generally it is in the range 20 to 40 or 45% by weight of the total mineral charge.

The melt will generally have a content of CaO in the range 10 to 40% and a content of MgO in the range 5 to 30% (often 7 to 20%). Generally the total amount of CaO plus  
25 alkali is 10 to 48% and the total amount of MgO + FeO is in the range 7 to 30%. The amount of SiO<sub>2</sub> is generally in the range 35 to 75%. Preferably the blend is such that the total alumina content is below 3% and often below 1%.

The blend can contain various compounds additional to the  
30 alumina, CaO, MgO, alkali and FeO and SiO<sub>2</sub> contents mentioned above. Thus it may contain other elements such as phosphorous, boron and titanium, generally each in an amount of not more than 10% measured as oxide.

It tends to be unsatisfactory to use briquettes which  
35 individually have a composition that is very high in silica and very low in CaO and/or MgO, particularly because such a briquette is likely to have a rather high melting point.

Accordingly it is preferred that substantially each briquette should have a content of  $\text{Al}_2\text{O}_3$  of 0 to 4%,  $\text{MgO}$  5 to 30% and  $\text{CaO}$  of 5 to 40%, all based on the weight of the briquette.

5       The desired chemical content may be achieved merely by mixing silica sand with olivine sand and a source of  $\text{CaO}$ , wherein generally all the sand is contaminated foundry sand but some could be uncontaminated sand. Often, however, the briquettes are formed from a blend of one or more  
10       contaminated foundry sands with other inorganic material, which may itself be industrial waste material. Suitable industrial waste materials include converter slag, glass, asbestos-free fibre cement, wood ash and steel plant dust and MMV fibre products, for instance bonded MMV fibrous  
15       material. This fibrous material may be recycled from the process or may be waste, previously manufactured, material.

      The charge to the furnace may consist solely of the briquettes containing contaminated foundry sand or, more usually, is a mixture of at least 30%, often at least 50%  
20       and typically up to 80% or more, of such briquettes with other particulate material. This other material may comprise briquettes made from materials free of contaminated foundry sand and/or other mineral material suitable for incorporation in the melt. This additional  
25       mineral material may be industrial waste, as discussed above, or may be virgin mineral material that has not previously been used.

      Such mineral material, that can be used as part of the non-briquette charge or as components in briquettes, can  
30       include materials such as dolomite, iron ore, limestone, rutile, magnesite, magnetite, brucite, burnt lime, slag and other materials suitable for forming a fibre-forming melt. The blend of contaminated foundry sand, other industrial waste and other mineral material should be such that the  
35       melt and the fibres have the desired composition.

      The briquettes may be made by any suitable method. Generally they are made by bonding inorganic material using

a binder, often associated with compression. The binder can be a hydraulic binder such as cement or may be a slag activated with an alkaline agent, as in WO92/04289. The binder may alternatively be a burnt lime which is hydrated  
5 on heating in the presence of water-the well known lime/sandstone process. Alternatively, the binder may be an organic binder, for instance a lignin binder obtained by mixing calcium lignosulphonate with the particulate material in the presence of water, allowing curing to start  
10 and then subjecting the partially cured mix to compression moulding, for instance on a roller moulding machine.

The use of organic binder is advantageous as it avoids the introduction of alumina or other inorganic component that might place an additional constraint on the materials  
15 that can be used in the charge.

The briquettes may have conventional dimensions, for instance a minimum dimension of at least 5mm, often at least 20mm and usually at least 40mm and a maximum dimension of up to 300mm but usually not more than around  
20 150 or 200mm.

The furnace may be heated in conventional manner, for instance as an electrical furnace or a tank furnace or, more usually by combustion of combustible material in a cupola furnace. The melt temperature will depend upon the  
25 minerals being used and the fibre-forming technique but is generally in the range 1200 to 1600°C, often around 1400 to 1550°C.

Fibre formation can be by conventional techniques such as a spinning cup technique or, preferably, by pouring on  
30 to a spinner comprising at least two co-operating spinning wheels, for instance as described in WO92/06047. Thus the fibres may be made by pouring the melt on to a first spinning rotor from which the melt is thrown in sequence on to one or more subsequent spinning rotors off which the  
35 fibres are thrown.

The products of the invention can be used for any of the conventional uses of MMV fibres, such as thermal



insulation, noise reduction and regulation, fire protection, growth media, reinforcement and fillers.

The following are some examples of the invention:

5     Example 1 100% briquette charge (85% industrial waste)

15% cement  
37% silica foundry sand  
19% olivine foundry sand  
29% converter slag

10

Example 2 100% briquette charge (57% industrial waste)

13% cement  
21% glass waste  
26% silica foundry sand  
10% olivine foundry sand  
21% dolomite  
9% iron ore

15

Example 3 100% briquette charge (63% industrial waste)

20     12% cement  
18% dolomite  
23% silica foundry sand  
10% olivine foundry sand  
10% glass waste  
25     20% mineral wool etc.  
7% iron ore

Example 4 89% briquette & 11% limestone (37% industrial waste)

30     Briquette composition:  
12% cement  
42% silica foundry sand  
46% dolomite

35     Example 5 100% briquette (60% industrial waste)

20% olivine  
31% silica foundry sand

31% limestone  
9% burnt lime

Example 6 100% briquette (54% industrial waste)

5        20% silica foundry sand  
         46% dolomite  
         14% glass waste  
         20% mineral wool etc.

10      Example 7 100% briquette (65% industrial waste)

         12% cement  
         36% silica sand  
         17% olivine sand  
         11% dolomite  
15       12% iron ore  
         12% mineral wool etc.

20       The chemical composition of the waste materials used  
         in the examples is shown in Table 1 and characteristics of  
         the charge and the products of each of the examples is  
         shown in Table 2.

TABLE 1

Chemical composition / Waste materials for soluble fibres

Sample	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	TiO <sub>2</sub> %	FeO %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	P <sub>2</sub> O <sub>5</sub> %	ZnO <sub>2</sub> %	MnO %
Foundry sand (silica sand)	98.6	1.4									
Foundry sand (olivine sand)	49.5			11.5		36.9					
Converter slag	11.1	1.6	1.7	25.3	49.1	2.1	0.1	0.1	2.9		
Waste glass	71.4	1.1	0.1	0.2	10.8	1.3	13.1	0.7			
Asbestos free fibre cement	20.3	3.2	0.2	1.5	41.4	5.3	0.5	0.2			
Wood ash	1.2			0.7	82.0	1.0		11.8	1.7		1.6
Steel plant dust	3.4			54.8	18.2	4.9	2.7	0.8		10.8	6.6

TABLE 2

## Characteristics of the examples

	Briquette amount in charge %	Industrial waste in charge %	Foundry sand * in charge %	Al <sub>2</sub> O <sub>3</sub> % in charge	CaO % in Charge	{CaO + alkali} % in charge	MgO % in charge	(MgO + FeO) % in charge
Example 1	100	85	56	1.6	25.4	25.9	10.5	17.1
Example 2	100	57	36	1.4	21.1	25.3	10.3	17.7
Example 3	100	63	33	2.0	21.1	23.6	12.6	19.5
Example 4	89	37	42	1.3	35.5	36.8	9.3	9.8
Example 5	100	60	60	0.6	25.6	26.0	18.0	19.7
Example 6	100	54	20	0.9	29.6	33.0	14.4	14.7
Example 7	100	65	53	3.2	16.3	17.4	12.3	19.2

\* Foundry sand: silica sand and olivine sand.

CLAIMS

1. A method of making man made vitreous fibres comprising forming moulded briquettes of particulate mineral material, forming a melt by melting in a furnace a charge comprising the briquettes and forming fibres from the melt, characterised in that the melt and the fibres have a content, measured as oxides, that includes  $\text{Al}_2\text{O}_3$  in an amount of not more than 4% by weight and the briquettes are formed of particulate material that includes contaminated foundry sand.
2. A method according to claim 1 in which the briquettes are formed of particulate material that includes contaminated foundry sand in an amount of at least 10% by weight based on the total mineral charge.
3. A method according to claim 1 or claim 2 in which the amount of contaminated foundry sand in the briquettes is 10 to 70% based on the weight of the total mineral charge.
4. A method according to any preceding claim in which substantially each of the briquettes has a content of  $\text{MgO}$  of 5 to 30% and a content of  $\text{CaO}$  of 5 to 40% by weight.
5. A method according to any preceding claim in which the melt and fibres has a content which includes 0 to 4%  $\text{Al}_2\text{O}_3$ , 10 to 40%  $\text{CaO}$ , 5 to 30%  $\text{MgO}$  and 25 to 75%  $\text{SiO}_2$ , and other oxides each in an amount of not more than 20%.
6. A method according to claim 5 in which the amount of  $\text{CaO}$  plus alkali is 10 to 48% and the amount of  $\text{MgO} + \text{FeO}$  is 7 to 30%.
7. A method according to any preceding claim in which the briquettes are formed additionally from other industrial waste selected from converter slag, glass, asbestos-free fibre cement, wood ash, steel plant dust and man made vitreous fibre products, wherein the total amount of contaminated foundry sand and other industrial waste is at least 50% based on the total mineral charge.
8. A method according to any preceding claim in which the furnace is a cupola furnace.

9. A process according to any preceding claim in which the fibres are made by pouring the melt on to a first spinning rotor from which the melt is thrown in sequence on to one or more subsequent spinning rotors off which the  
5 fibres are thrown.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/02109

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C13/06 C03C1/00 C03C1/02 C03B1/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO-A-92 04289 (PAROC OY AB) 19 March 1992 cited in the application see page 2, line 4 - line 27; claims 1-10 ---	1-9
A	PATENT ABSTRACTS OF JAPAN vol. 5 no. 12 (C-040) ,24 January 1981 & JP,A,55 140725 (HIYUGOKEN) 4 November 1980, see abstract -----	1-3,7



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Date of the actual completion of the international search

12 September 1995

Date of mailing of the international search report

06.10.95

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### Information on patent family members

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Formo PCT/ISA/210 (patent family annex) (July 1992)